

Abatement of fluoride from water using manganese dioxide-coated activated alumina

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Abstract

Batch adsorption of fluoride onto manganese dioxide-coated activated alumina (MCAA) has been studied. Adsorption experiments were carried out at various pH (3–9), time interval (0–6 h), adsorbent dose (1–16 g/l), initial fluoride concentration (1–25 mg/l) and in the presence of different anions. Adsorption isotherms have been modeled using Freundlich, Langmuir and Dubinin–Raduskevich isotherms and adsorption followed Langmuir isotherm model. Kinetic studies revealed that the adsorption followed second-order rate kinetics. MCAA could remove fluoride effectively (up to 0.2 mg/l) at pH 7 in 3 h with 8 g/l adsorbent dose when 10 mg/l of fluoride was present in 50 ml of water. In the presence of other anions, the adsorption of fluoride was retarded. The mechanism of fluoride uptake by MCAA is due to physical adsorption as well as through intraparticle diffusion which was confirmed by kinetics, Dubinin–Raduskevich isotherm, zeta-potential measurements and mapping studies of energy-dispersive analysis of X-ray.

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1. Introduction

Extensive research has been done on removal of fluoride from aqueous solution due to the adverse effect it causes to human body. Several methods such as adsorption [1–6], precipitation [7,8], ion exchange [9,10], reverse osmosis [11], nanofiltration [12], Donnan dialysis [13,14] and electro dialysis [15,16] techniques have been used for defluoridation. In 1979, Bulusu et al. [17] developed the Nalgonda technique, in which aluminum salt is added along with lime to fluoride-contaminated water to form flocs. The flocs (aluminum hydroxide) in turn remove fluoride by sorption or by co-precipitation. Use of calcite to remove fluoride from aqueous solution by precipitation method has been investigated by many authors [7,8,18]. Reardon and Wang [7] studied fluoride removal using a lime stone reactor where the dissolution of calcite occurred to form CaF_2 precipitate. Fluoride removal by calcite was studied by Turner et al. [8] and they found that along with the precipitation reac-

tion, adsorption of fluoride also occurs which was confirmed by atomic force microscopy, X-ray photoelectron spectroscopy and zeta-potential studies.

Adsorption process has been widely used, in which various adsorbents, viz. activated alumina [19,20], activated carbon [21], low-cost adsorbents [5,22–24], rare earth oxides [1], natural products [22,23] like tree bark, groundnut husk, sawdust, rice husk, etc., have been utilized. In connection with our research program on defluoridation, we have reported earlier the sorption behavior of fluoride on rare earth oxides [1], natural adsorbents [22,23] and impregnated oxides [24].

In 2001, Raichur and Basu [1] investigated adsorption of fluoride onto mixed rare earth oxides to study the effectiveness of these mixed rare earth oxides towards fluoride removal. They found that 98.5% of fluoride has been removed from synthetic solution at pH 6.7 and 8 g/l of mixed rare earth oxide. In an earlier work, Srivastava et al. [23] and Tripathy et al. (2004) [22] studied the removal of fluoride from water using sawdust, groundnut husk and sand. The results obtained indicate that these chemically treated natural adsorbents remove fluoride effectively. Activated alumina is known to be a very good adsorbent due to its high surface area, crystalline form, and activation

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process [21]. But usually it works effectively at pH below 6 [24,25].

In recent years, a considerable amount of work has been done on impregnation of oxides and natural adsorbents with chemicals to improve the adsorption capacity and hence removal efficiency [28–31]. Aluminum-impregnated carbon [21], lanthanum oxide-coated silica gel [26], La³⁺-impregnated cross-linked gelatin [27] and zirconium(IV)-impregnated collagen fiber [28] were reported to be very effective for defluoridation. The influence of impregnation of aluminum on activated carbon was investigated by Ramos et al. (1999) [21]. They found that impregnated activated carbon has three to five times more adsorption capacity than that of plain activated carbon. In a further study of our previous work [22,24], we have examined the adsorption behavior of chemically impregnated oxides and sands including alum-impregnated activated alumina for removal of fluoride from water. We found that alum-impregnated activated alumina performed better as compared to activated alumina for defluoridation of water. It was observed that up to 0.2 mg/l fluoride could be removed by alum-impregnated activated alumina. Maliyekkal et al. [25] studied the removal of fluoride using manganese oxide-coated alumina (MOCA). They found that MOCA is an effective adsorbent for defluoridation of water when initial concentration of fluoride in water is 5 mg/l.

In this paper, the effect of manganese dioxide coating on activated alumina on removal of fluoride as compared to uncoated activated alumina is reported. An attempt has been made to elucidate the uptake mechanism of fluoride using manganese dioxide-coated activated alumina. Studies have been carried out to determine the adsorption kinetics, adsorption isotherm, effect of pH and adsorbent dose on the efficacy of manganese dioxide-coated activated alumina towards removal of fluoride. The sorption behavior of fluoride on the adsorbent was investigated by zeta-potential and EDAX studies to understand the solid/liquid interface phenomena.

2. Materials and methods

2.1. Chemicals

All the chemicals used were of analytical grade (E. Merck, India). Double distilled water was used in all the experiments. All the experiments were carried out at room temperature and atmospheric pressure. Synthetic fluoride stock solution was prepared by adding appropriate quantity of sodium fluoride to distilled water and was used for adsorption experiments after appropriate dilution.

2.2. Preparation of manganese dioxide-coated activated alumina

The activated alumina was coated [29] with manganese dioxide as follows: 26.675 g of KMnO₄ was dissolved in 2 l of distilled water in a beaker and kept in a water bath at 90 °C for 15 min. Twenty-four grams of activated alumina was added to this solution and mixed gently. The suspension was kept in the water bath for 10 min. Then 300 ml of 2 M HCl was added to that

suspension and mixed thoroughly and again kept in the water bath for 30 min. After completion of the reaction the solid was cooled and washed with distilled water and 0.05 M perchloric acid until the runoff was clear. Finally it was dried at ambient temperature and stored in a sorbent bottle. This manganese dioxide-coated activated alumina is referred as MCAA.

2.3. Characterization of manganese dioxide-coated activated alumina

The specific surface area was determined by the low-temperature N₂ absorption method. The particle size distribution of the MCAA was measured by using a Malvern Master Sizer. The isoelectric point of activated alumina, MCAA and the fluoride-adsorbed MCAA was determined by measurement of zeta-potential of the particles (Malvern Zeta-sizer Model 3000, UK). Scanning electron microscopy (SEM) and energy-dispersive analysis of X-ray (EDAX) were performed using a FEI SIRION (20 kV) scanning electron microscopy.

2.4. Adsorption of fluoride by manganese dioxide-coated activated alumina

All the adsorption experiments were carried out in batch mode. A known quantity of MCAA and desired concentration of fluoride solutions were taken in a 100 ml Teflon-coated bottle. The pH of the solution was adjusted by using dilute HCl or NaOH solution.

The final volume was made up to 50 ml with distilled water. The experimental procedure for adsorbent dose (0.5–16 g/l), effect of pH (3–9), adsorption kinetics (0–6 h) and isotherm (1–25 mg/l) studies has been described in our earlier paper [24]. The interference of ions on fluoride adsorption was carried out in the same manner as mentioned for other parameters at different concentration (25–100 mg/l) of ions. The filtrate was analyzed for residual fluoride concentration by using a UV–vis spectrophotometer (Thermo Electron-T 60, UK) using SPADNS reagent at 570 nm, outlined in the Standard Methods of Examination of Water and Wastewater [30].

3. Results and discussion

3.1. Characterization of manganese dioxide-coated activated alumina

The scanning electron micrographs of activated alumina and MCAA are shown in Fig. 1a and b, respectively. In Fig. 1b small particles can be seen adhering to the AA surface. The surface area, pore volume, particle size and isoelectric point of AA and MCAA are given in Table 1. The decrease in surface area of MCAA indicates that diffusion of manganese dioxide takes place into the pores of the AA surface, which is further confirmed from the pore volume measurements. But in case of alum-impregnated activated alumina, it is observed that surface area increased upon impregnation due to the uniform coating of Al(OH)₃ on activated alumina surface [24].

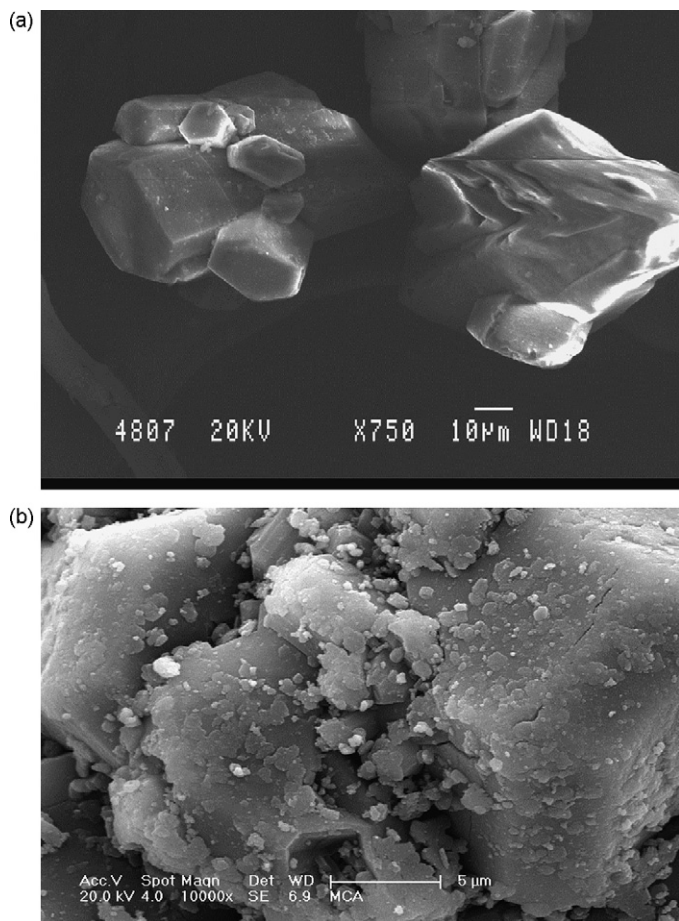


Fig. 1. (a) SEM micrograph of activated alumina. (b) SEM micrograph of manganese dioxide-coated activated alumina.

Table 1
Properties of activated alumina and MCAA

Properties	Activated alumina (AA)	Manganese dioxide-coated activated alumina (MCAA)
Particle size, d_{50} (μm)	82	87
Surface area (m^2/g)	242	203
Pore volume (cm^3/g)	0.39	0.23
Isoelectric point	8.3	7.7

3.2. Zeta-potential measurements

Fig. 2 shows the zeta-potential versus pH of AA and MCAA in 1×10^{-2} M KNO_3 solutions. It was found that the isoelectric point (IEP) of AA was at pH 8.3 with the surface being positively charged below the IEP and negatively charged above the IEP. The IEP value of MnO_2 as such is known to be 2.1. The IEP of MCAA was found to be 7.7 which is lower compared to that of AA. The shift in IEP value from 8.3 to 7.7 was probably due to the adsorption of manganese dioxide on the surface of AA and hence the presence of MnO_2 on the surface decreases the IEP of MCAA towards it.

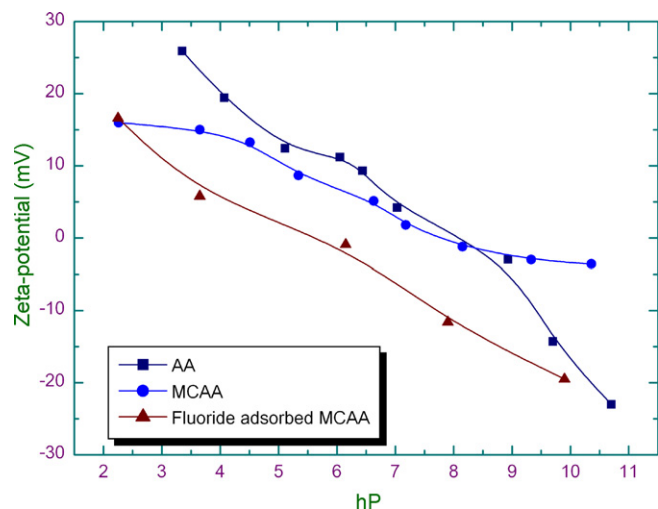


Fig. 2. Zeta-potential of activated alumina, manganese dioxide-coated activated alumina and fluoride-adsorbed manganese dioxide-coated activated alumina at an ionic strength of 0.01 M KNO_3 solution.

3.3. Effect of pH

The role of pH is a major factor which controls the adsorption at the water-adsorbent interface as described in our earlier papers [1,24]. Fig. 3 shows the adsorption of fluoride onto AA and MCAA as a function of pH. Adsorption of fluoride onto AA increased with increasing pH and reached a maximum of 87% at pH 5.5 but decreased with further increase in pH. In case of MCAA, initially the adsorption of fluoride increased from pH 3 to 5.5 reaching a maximum of 99% at pH 5.5 after which a slight decrease to 98% at pH 7 was observed. There after the adsorption of fluoride decreased sharply and only 64% of fluoride was adsorbed at pH 9. The advantage of coating AA is that the adsorption of fluoride occurs over a wide range of pH, i.e. pH 3–7 whereas the maximum adsorption in case

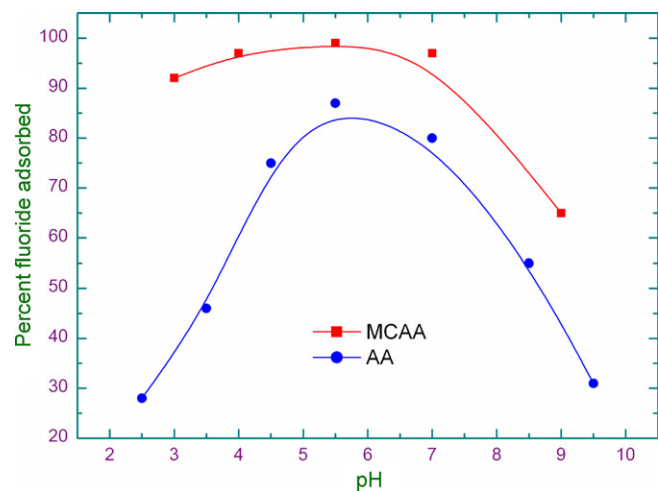


Fig. 3. The plot of percent removal of fluoride onto AA and MCAA as a function of pH at adsorbent dose 8 g/l, fluoride concentration 10 mg/l and equilibrium time 3 h.

of activated alumina took place at pH 5.5. Also, adsorption was always higher at any given pH for MCAA when compared to AA. Moreover, on addition of the coated AA to water, the resultant pH of the solution was automatically set to around 7. Therefore, the addition of any acid/alkali is not necessary during the adsorption process. This will have an implication in the treatment of drinking water where the natural pH is around 7 and no additional pH adjustments are required to be done. Therefore manganese dioxide-coated activated alumina has a greater potential to be used for treating fluoride-contaminated drinking water. In depth studies have been done to establish the mechanism of adsorption of fluoride onto coated activated alumina which is discussed in the following sections.

3.4. Adsorption kinetics

The uptake of fluoride onto MCAA was studied at different time intervals. Adsorption of fluoride increased with time and it was fast in the first 10–60 min. Then the adsorption rate decreased and attained equilibrium at 3 h. A maximum of 98% fluoride was adsorbed in 3 h after which there was no significant

adsorption. Therefore, 3 h was the optimum time required for maximum adsorption of fluoride.

The reaction kinetics of pseudo-first-order and pseudo-second-order was investigated by using the results obtained from the adsorption of fluoride at different time intervals.

Pseudo-first-order rate expression of Lagergen equation [31] is given as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

The integrated and logarithmic form of the above equation is written as

$$\log(q_e - q_t) = \log q_e - k_1 t \quad (2)$$

where q_e and q_t are the amount of fluoride adsorbed on the adsorbent at equilibrium (mg/g) and at time t (min), respectively and k_1 is the rate constant of the pseudo-first-order adsorption (min^{-1}).

The adsorption rate constant can be determined from the slope of the linear plot of $\log(q_e - q_t)$ versus t (Fig. 4a). k_1 and the correlation coefficient R^2 were found to be 0.0045 and 0.7658,

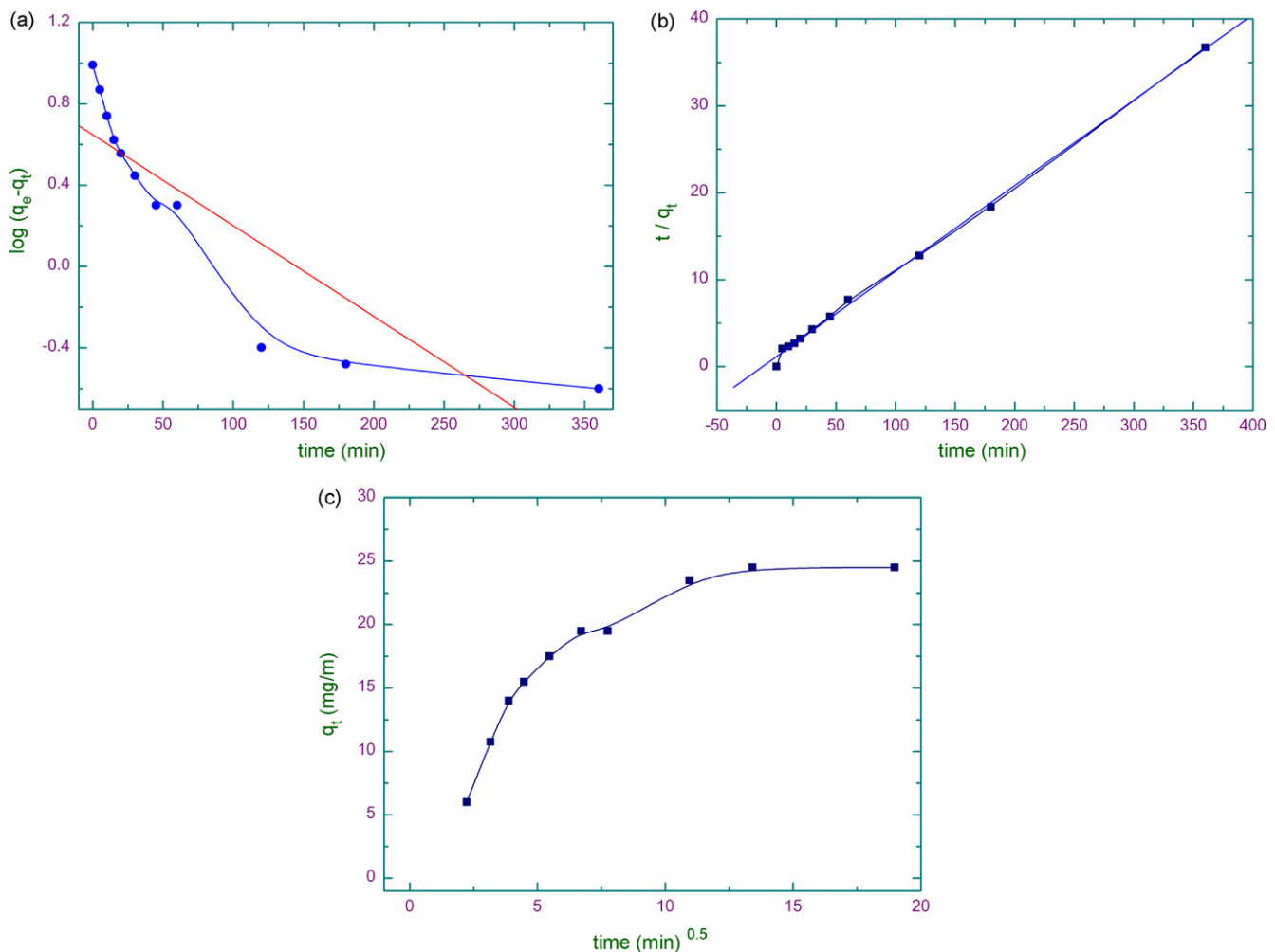


Fig. 4. (a) Pseudo-first-order plot of fluoride adsorption kinetics at pH 7, 8 g/l adsorbent dose and an initial fluoride concentration of 10 mg/l. (b) Pseudo-second-order plot of fluoride adsorption kinetics at pH 7, 8 g/l adsorbent dose and an initial fluoride concentration of 10 mg/l. (c) Intraparticle diffusion plot for adsorption of fluoride onto MCAA at pH 7, 8 g/l adsorbent dose and an initial fluoride concentration of 10 mg/l.

respectively which are extremely low. It is known that the larger the k_1 value, the quicker the adsorption rate. Therefore, from the very low values of k_1 and R^2 obtained from Fig. 4a, it can be concluded that the adsorption of fluoride onto manganese dioxide-coated activated alumina does not follow first-order rate model.

The pseudo-second-order rate expression is as follows [32]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

$$\Rightarrow \frac{d(q_e - q_t)}{(q_e - q_t)^2} = -k_2 dt \quad (4)$$

Integrating Eq. (4) at $t=0$ to $t=t$ and $q_t=0$ to $q_t=t$, which gives

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (5)$$

$$\Leftrightarrow \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

k_2 is the pseudo-second-order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$).

From Eq. (6), k_2 can be calculated from the slope and intercept of the plot t/q_t versus t (Fig. 4b). The larger the k_2 value, the slower the adsorption rate. The value of k_2 and R^2 for the pseudo-second-order rate model is found to be $0.0083 \text{ g mg}^{-1} \text{min}^{-1}$ and 0.9989. The low k_2 and extremely high R^2 value suggest that the adsorption is governed by pseudo-second-order model.

3.4.1. Intraparticle diffusion

In spite of adsorption occurring on the surface of adsorbent, the adsorbate molecules may also diffuse into the interior of the porous of the adsorbent. The existence of intraparticle diffusion in the adsorption process can be determined from the following equation [33]:

$$q_t = k_i t^{1/2} \quad (7)$$

where k_i is the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-1/2}$) calculated from Eq. (7).

Fig. 4c shows the amount of fluoride adsorbed (q_t) versus the square root of time ($t^{1/2}$). If the correlation of the above variables gives straight line that passes through the origin, then it suggests that the intraparticle diffusion contributes predominantly in rate determining step for the adsorption [33]. Fig. 4c shows that the initial portion of the curve gives a straight line, which implies during the initial time up to 15 min, the adsorption model follows intraparticle diffusion. After 15 min, it does not follow intraparticle diffusion. After this, surface adsorption may be the predominant mechanism of fluoride uptake. The unusual behavior is obtained due to the heterogeneous nature of MCAA surface. Therefore, the adsorption of fluoride onto MCAA is both through surface adsorption as well as intraparticle diffusion effect.

3.5. Effect of adsorbent dose

Fig. 5a shows the effect of adsorbent dose on the removal of fluoride at pH 7.0 and initial fluoride concentration of 10 mg/l

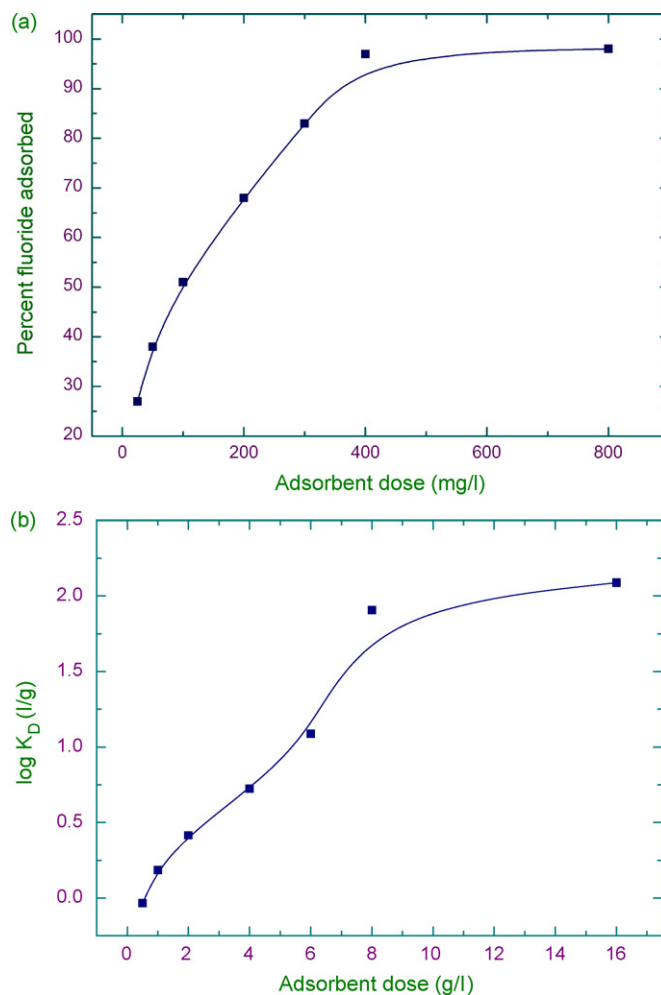


Fig. 5. (a) The plot of percent removal of fluoride as a function of adsorbent dose (g/l) onto MCAA at fluoride concentration 10 mg/l, pH 7 and equilibrium time 3 h. (b) The plot of $\log K_D$ value as a function of adsorbent dose (g/l).

for 3 h. It can be seen from Fig. 5a that the adsorption of fluoride depends on the amount of adsorbent added. Initially, at 0.5 g/l of the adsorbent dose, 27% of fluoride is removed and gradually increases up to 98.2% at 8 g/l of adsorbent. Thereafter the adsorption of fluoride remained constant which indicates that 8 g/l adsorbent is sufficient to remove 10 mg/l of fluoride. A similar trend was also observed in case of alum-impregnated activated alumina in our previous work [24]. Due to the increase in active sites of adsorbent with increasing dosage, the adsorption of fluoride also increases.

The binding ability of an adsorbent surface for an element can be determined from the distribution coefficient, K_D which was calculated as follows

$$K_D = \frac{C_S}{C_W} \quad (8)$$

where C_S is the concentration of fluoride on the solid particles (mg/kg) and C_W is the equilibrium concentration in water (mg/m^3).

The distribution coefficient K_D , increases with increasing adsorbent dose which is depicted in Fig. 5b. This increase trend in K_D value implies that the surface of MCAA is heterogeneous

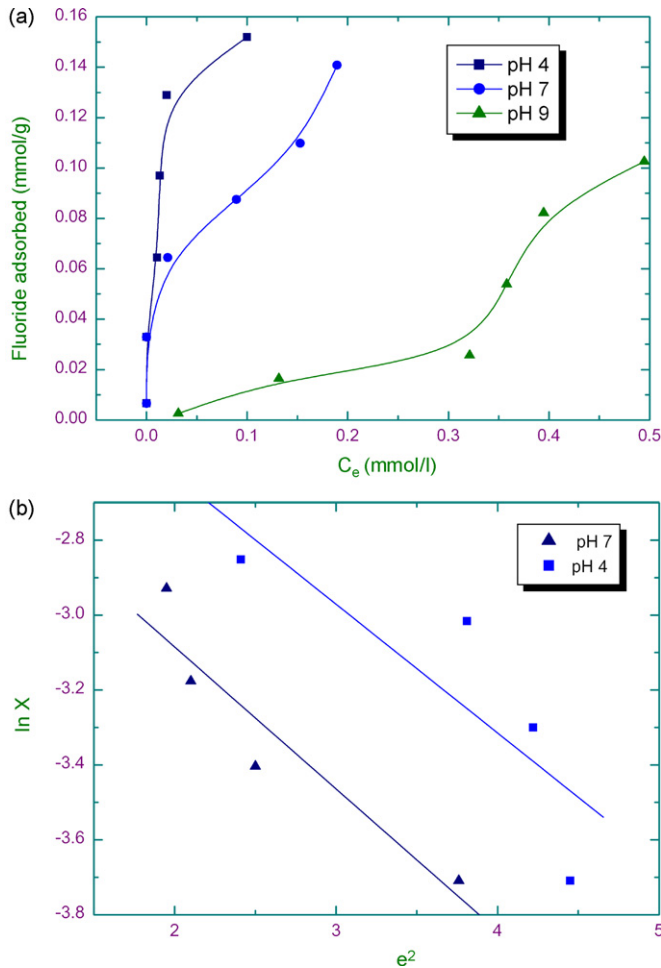


Fig. 6. (a) Adsorption isotherm of fluoride onto MCAA at pH 7, adsorbent dose 8 g/l, equilibrium time 3 h. (b) Dubinin–Radushkevich type adsorption isotherm of fluoride onto MCAA.

in nature. For a homogeneous surface, the K_D value at a given pH should not change with adsorbent concentration [34].

3.6. Equilibrium studies and adsorption isotherm

Equilibrium studies were carried out at three pH values 4, 7 and 9 by varying fluoride concentration range from 1 to 25 mg/l. Fig. 6a illustrates the adsorption isotherm of fluoride which indicates that adsorption of fluoride increases with increasing equilibrium concentration and with decreasing pH. Adsorption is very high at pH 4 and 7. In contrast, at pH 9 adsorption is low at low equilibrium concentration and increases only at high C_e values.

Table 2
Adsorption isotherms of fluoride onto MCAA

pH	Langmuir isotherms			Freundlich isotherms			D–R isotherms		
	Q (mg/g)	b (l/mg)	R^2	k	$1/n$	R^2	X_m (mol/g)	K (mol ² /kJ ²)	R^2
4	0.1701	87.99	0.9944	8.45	0.32	0.9491	0.0019	0.3436	0.6996
7	0.1591	20.29	0.9472	8.90	0.31	0.8206	0.0023	0.3792	0.8782

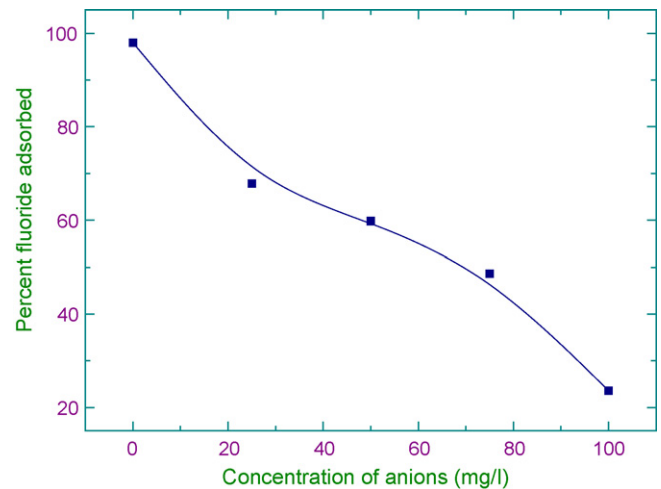


Fig. 7. Effect of interfering ions in the adsorption of fluoride.

Adsorption isotherm data were fitted to both Langmuir and Freundlich isotherm to know the distribution between adsorbent and adsorbate interface at equilibrium. As the adsorption of fluoride at pH 9 is low compared to that at pH 4 and 7, it was not considered for isotherm studies.

The Freundlich isotherm [2], which is an indicative of the surface heterogeneity of the adsorbent, is given as follows

$$\ln\left(\frac{x}{m}\right) = \ln k + \frac{1}{n} \ln C \quad (9)$$

where k and $1/n$ are temperature-dependent Freundlich constants related to adsorption capacity and adsorption intensity, respectively, C the equilibrium concentration (mg dm⁻³) and x/m is the amount adsorbed at equilibrium (mg/g).

By plotting as $\ln q$ against $\ln C$, the k and n values can be obtained from the slope and intercept value. The values obtained from the Freundlich plot is given in Table 2.

The Langmuir isotherm [2] which is valid for the monolayer adsorption onto the adsorbent surface for the adsorption of fluoride from aqueous solution is given by

$$\frac{C}{x/m} = \frac{C}{Q} + \frac{1}{bQ} \quad (10)$$

where C is the equilibrium concentration (mg dm⁻³), x/m the amount adsorbed at equilibrium (mg/g) and Q and b are the Langmuir constants related to the capacity and energy of adsorption, respectively.

The Langmuir constants Q and b can be determined from the linear plot of $C/(x/m)$ versus C , which is given in Table 2.

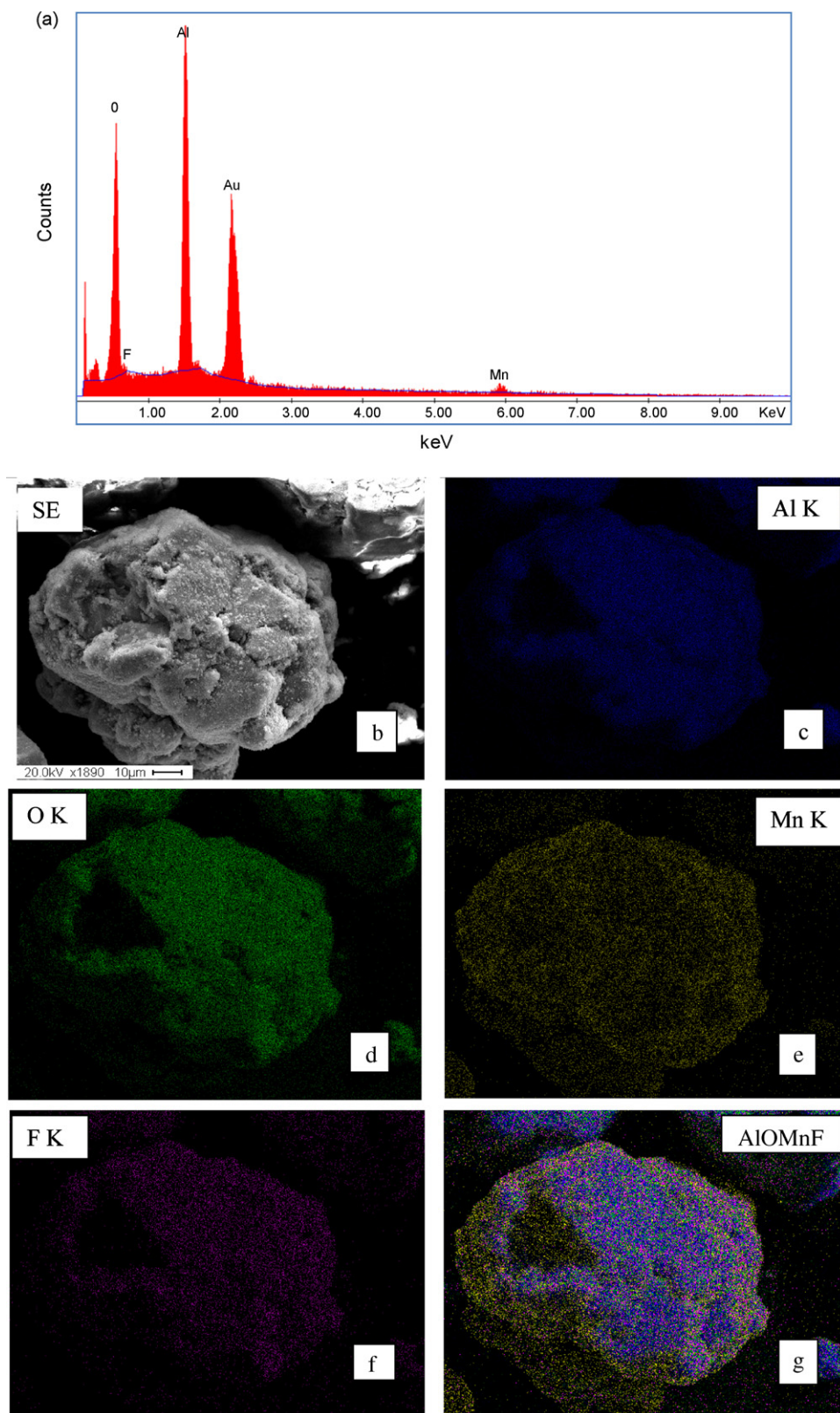


Fig. 8. (a) EDAX spectrum of fluoride-adsorbed MCAA. (b)–(g) EDAX Mapping of fluoride-adsorbed MCAA.

3.6.1. Dubinin–Radushkevich isotherm

Though the Freundlich and Langmuir isotherm models are widely used, but these models do not give any idea about the

adsorption mechanism. Therefore, to develop the mechanism of adsorption process, the equilibrium data were tested with the Dubinin–Radushkevich isotherm model (D–R isotherm) [35].

Dubinin–Raduskevich model predicts the sorption nature of the adsorbate on adsorbent and it is used to calculate the mean free energy of sorption.

D–R equation can be written as

$$X = X_m \exp(-K\varepsilon^2) \quad (11)$$

where ε (polanyi potential) = $RT \ln(1 + (1/C))$, X the amount of fluoride adsorbed per unit weight of adsorbent (g g^{-1}), X_m the adsorption capacity (g g^{-1}), C the equilibrium concentration of fluoride in aqueous solution (g/l), K the constant related to the adsorption energy, R the gas constant and T is the temperature (K).

D–R isotherm can be linearized by logarithmic transfer of both sides:

$$\ln X = \ln X_m - K\varepsilon^2 \quad (12)$$

D–R isotherm constants, K and X_m can be calculated from the slope and intercept of the plot of $\ln X$ against ε^2 , respectively (Fig. 6b), which is given in Table 2. The mean free energy of adsorption (E), defined as the free energy change when 1 mol of ion is transferred to the surface of the solid from infinity in solution can be calculated from the K -value obtained from the above equation [36]:

$$E = (-2K)^{-0.5} \quad (13)$$

From the magnitude of E , the type of adsorption such as chemisorption or physical sorption can be determined. If $E = 8\text{--}16 \text{ kJ mol}^{-1}$, then the reaction is due to the chemisorption; If $E < 8 \text{ kJ mol}^{-1}$, then physical type of sorption takes place.

The mean free energy of adsorption (E) is found to be $1.206 \text{ kJ mol}^{-1}$ for pH 4 and 1.15 kJ mol^{-1} for pH 7, which implies that the adsorption of fluoride on MCAA is purely by physical adsorption.

3.7. Effect of different anions

Usually in water many ions such as sulfate, phosphate, chloride and nitrate are present and these compete with fluoride ions during adsorption. So the effect of these ions on adsorption of fluoride onto MCAA was carried out. The initial concentration of fluoride was fixed (10 mg/l) whereas the concentration ($25\text{--}100 \text{ mg/l}$) of sulfate, phosphate, chloride and nitrate was varied in the adsorption test. Fig. 7 shows the different concentration of anions versus percent fluoride adsorbed. It can be seen from the figure that the adsorption of fluoride decreases with increase in anions concentration. At 0 mg/l of ions, fluoride adsorbed is 98% while the adsorption of fluoride reduced to 25% at 100 mg/l of anions.

3.8. Evidence in support of adsorption of fluoride on MCAA

3.8.1. EDAX analysis

Energy-dispersive analysis of X-rays was used to analyze the elemental constituents of fluoride-adsorbed MCAA. Fig. 8a shows the presence of fluoride in small amounts in the spectrum

along with the principal elements Al and O and minor elements like Mn. The Mn peak is observed due to the coating of manganese dioxide on AA. Presence of a minor peak for fluoride in Fig. 8a indicates that fluoride is superficially adsorbed on MCAA surface. Fig. 8b shows the scanning electron micrograph of fluoride adsorbed onto MCAA. EDAX mapping (done by secondary electron scattering) was carried out for each element present in the fluoride-adsorbed MCAA. Fig. 8c–f shows the presence of Al, O, Mn and F in bulk amount and Fig. 8g shows the overlapped image of the four elements. A significant amount of fluoride is present on the surface which provides direct evidence of fluoride adsorbed onto the surface of MCAA. On careful observation, it can be seen that the images of Al, O and F are almost same (Fig. 8c, d and f) whereas the image of Mn is different. This indicates that most of the fluoride is adsorbed onto the alumina than on the manganese dioxide as discussed earlier.

3.8.2. Zeta-potential measurement

Zeta-potential measurement was performed with fluoride-adsorbed MCAA in 10^{-2} M KNO_3 solutions. From Fig. 2 it can be seen that the IEP value of fluoride-adsorbed MCAA was found to be 5.9. It is known that the surface of the fluoride-adsorbed MCAA is negatively charged and hence the zeta-potential value is expected to be more negative than the as such MCAA. Therefore, the shift in IEP to the lower value, i.e. from 7.7 to 5.9 provides direct evidence that fluoride is adsorbed on the surface of MCAA.

4. Conclusions

Manganese dioxide-coated activated alumina has been shown to be a promising adsorbent for enhanced defluoridation of water as compared to uncoated activated alumina. Coated activated alumina adsorbed more fluoride than uncoated one over a wider pH range. More importantly maximum adsorption occurred at around pH 7 in case of coated alumina which makes it a potential adsorbent for treating drinking water. Kinetics studies reveal that adsorption of fluoride follows second-order rate law. From the intraparticle diffusion study it can be concluded that the adsorption was due to both surface adsorption as well as through intraparticle diffusion. The equilibrium data were fitted to Freundlich, Langmuir and Dubinin–Raduskevich isotherm model. Langmuir isotherm model fitted well to this system. Mean free energy value of adsorption obtained from Dubinin–Raduskevich isotherm model suggests that physical adsorption plays an important role in adsorption process. Manganese dioxide-coated activated alumina could remove fluoride up to 0.2 mg/l when the initial concentration of fluoride in water is 10 mg/l . However, the adsorption of fluoride decreases in presence of other ions. Regeneration study reveals that re-coating of manganese dioxide is needed for further use as adsorption capacity of MCAA decreases after first use. Zeta-potential measurement and EDAX analysis and EDAX mapping studies suggest that fluoride adsorption onto MCAA occur through mostly surface adsorption.

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